

PATENT ABSTRACTS OF JAPAN

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(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte secondary battery having a good productivity and a high capacity by shortening and the time required for an electrolyte filling an aging process.

SOLUTION: In a nonaqueous electrolyte secondary battery having an electrode group that is wound or stacked sheet-shaped positive electrodes 1 and sheet-shaped negative electrodes 2 via separators 3a cavity in a battery after filling electrolyte is not more than 10% of a battery inside volumeand moreover density of the electrolyte is not less than 1.35 g/cc. Accordinglyit is possible to provide the nonaqueous electrolyte secondary battery which can shorten the time required for an electrolyte filling process and an aging processand which has excellent productivity and a high capacity.

CLAIMS

[Claim(s)]

[Claim 1] In a nonaqueous electrolyte secondary battery which has the electrode group which wound or laminated a sheet shaped anode and a sheet shaped negative electrode via a separator A nonaqueous electrolyte secondary battery wherein an opening in a cell after electrolysis solution pouring is 10% or less of cell content volume and density of an electrolysis solution is not less than 1.35g/cc.

[Claim 2] The nonaqueous electrolyte secondary battery according to claim 1 which viscosity contained by 4 or less cp density made contain a not less than 1.40g/cc solvent not less than 20% by a volume ratio in an electrolysis solution and density used as a not less than 1.35g/cc electrolysis solution.

[Claim 3] The nonaqueous electrolyte secondary battery according to claim 1 or 2 whose pack density of a negative electrode mixture layer of a negative electrode is more than 1.5 g/cm³.

[Claim 4] The nonaqueous electrolyte secondary battery according to claim 1 or 2 whose pack density of a positive electrode mixture layer of an anode is more than 3.3 g/cm³.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] About a nonaqueous electrolyte secondary battery in more detail this invention is excellent in productivity and relates to the nonaqueous electrolyte secondary battery of high capacity.

[0002]

[Description of the Prior Art] Production has expanded rapidly the nonaqueous electrolyte secondary battery represented by the lithium secondary battery recently from it being high capacity and their being high tension and high energy

density.

[0003] Although lithium or a lithium alloy is conventionally used as negative electrode active material of a nonaqueous electrolyte secondary battery, these days the nonaqueous electrolyte secondary battery using black lead, difficulty graphitized carbon system material, etc. as negative electrode active material is put in practical use using lithium transition metal compound, such as LiCoO_2 , as positive active material.

[0004] In this nonaqueous electrolyte secondary battery, after an anode and a negative electrode apply and dry on a substrate the mixture content paste which distributed and prepared the active material to the organic solvent with an electric conduction auxiliary agent, a binder, etc. which are added if needed and provide a binder layer, it is produced by rolling to given thickness. And wind or laminate this anode and negative electrode via a separator and it is considered as an electrode group. After inserting this in a cell case, the electrolysis solution of a nonaqueous solvent system which used the organic solvent as the main solvent is poured in and it obturates with an obturation object and by carrying out predetermined time aging, an electrolysis solution is made to permeate the whole binder layer and it is changing into the state in which charge and discharge are possible.

[0005]

[Problem(s) to be Solved by the Invention] By the way, since the electrode of a nonaqueous electrolyte secondary battery is a coating mold electrode which applies to a substrate the mixture content paste made into paste state, dries, and produces an active material, etc. with an organic solvent as mentioned above, in order to obtain desired cell capacity at the time of charge and discharge, an electrolysis solution fully permeates between the active material particles in a binder layer and all the active materials in a binder layer need to contribute to electrochemical reaction.

[0006] On the other hand, when high-capacity-izing this nonaqueous electrolyte secondary battery while increasing the volume of an electrode, it is necessary to raise the pack density of the binder layer of the anode and negative electrode

which are provided on a substrate to lessen the opening in a cell such as also increasing the injection rate of an electrolysis solution as much as possible and to make [many / as possible] the rate that a power generation element occupies to cell content volume.

[0007] And when making pack density of a binder layer high as for more than 2.5 g/cm³ in the positive electrode mixture layer carrying out pack density in a negative electrode mixture layer more than 1.0 g/cm³ is proposed in pack density (JP4-345361AJP5-290848A).

[0008] However in the nonaqueous electrolyte secondary battery using the electrode group which enlarged volume of the electrode as mentioned above and made pack density high. Since the voidage in a binder layer is also small while a long time is needed when pouring in the predetermined amount of electrolysis solutions since there are few openings in a cell a long time is needed also for the aging process after the assembly process performed in order to make an electrolysis solution permeate a binder layer.

[0009] In order to attain especially high capacity-ization when the opening in the cell after electrolysis solution pouring is lessened with 20% or less of cell content volume the electrolysis solution of the specified quantity cannot be poured in at once at the time of electrolysis solution pouring but it side-** from a cell case. Therefore it is necessary to divide and pour pouring of an electrolysis solution into multiple times taking into consideration the infiltration speed of the electrolysis solution to a binder layer. And in the manufacturing process of a nonaqueous electrolyte secondary battery since the implantation process and the aging process of an electrolysis solution serve as a rate determining step it is anxious for shortening these processes as much as possible in mass production.

[0010] Therefore an object of this invention is to shorten the time which the electrolysis solution implantation process and the aging process at the time of attaining high capacity-ization as mentioned above take and for productivity to be excellent and to provide the nonaqueous electrolyte secondary battery of high capacity.

[0011]

[Means for Solving the Problem] Even when this invention is made as a result of [which should solve an aforementioned problem] inquiring wholeheartedly and an opening in a cell after electrolysis solution pouring is made into 10% or less of cell content volume by making density of an electrolysis solution high in cc and not less than 1.35g / An electrolysis solution's own perviousness is raised time which an electrolysis solution implantation process and the aging process take is shortened and productivity is excellent and a nonaqueous electrolyte secondary battery of high capacity is obtained.

[0012]

[Embodiment of the Invention] When the above-mentioned density prepares a not less than 1.35g/cc electrolysis solution and viscosity makes the solvent of 4 or less cp contain the perviousness of an electrolysis solution can improve further and the time which an electrolysis solution implantation process and the aging process take can be shortened further.

[0013] It is as follows when the progress which came to complete this invention is explained in detail.

[0014] First when this invention person used the conventional electrolysis solution and the cause which an electrolysis solution implantation process and the aging process long-time-ize was examined it became clear that the density of an electrolysis solution had influenced greatly. Namely although ester ether and carbonate are used as a main solvent and it is prepared by dissolving electrolyte such as LiPF_6 in these mixed solvents in the conventional electrolysis solution Even when high [that density is low and] in about 1.20g/cc it is about 1.30g/cc and it became clear from the lowness of this density that the infiltration speed of an electrolysis solution became slow.

[0015] Then when the time which pouring of an electrolysis solution takes by making density of an electrolysis solution higher than cc not less than 1.35g / and the former can be shortened in this invention and viscosity makes the solvent of 4 or less cp especially contain in an electrolysis solution It found out that the time

which aging takes could also be shortened substantially.

[0016]In this invention although the opening in the cell after electrolysis solution pouring is targeting 10% or less of cell of cell content volume In order that this may obtain the nonaqueous electrolyte secondary battery of high capacity the fill ration of a power generation element is made [many / as possible] Since the electrolysis solution in which an opening cannot fully permeate the binder layer of an electrode in a cell more than 10% at the time of pouring of an electrolysis solution in a certain case is temporarily stored in the gap part an opening can obturate immediately but. It is because obturation is impossible unless it comes out of from [after making an electrolysis solution fully permeate over many hours] since the electrolysis solution which cannot permeate a binder layer overflows from a cell case when the opening in a cell is lessened with 10% or less of cell content volume so this invention is needed.

[0017]In this invention the capacity which cell content volume said the total volume formed in that inside when the opening of a cell case was obturated therefore the power generation element etc. occupy is also contained in this cell content volume. It can ask for the capacity of the opening in a cell as follows.

[0018]** A cell is put into a measuring cylinder etc. and the solvent of known volume is added from on the and let volume of the portion which increased from the volume of the solvent be cell total volume.

** Open a cell case within a glove box and measure volume similarly in the state where a solvent may permeate an inside. [Since an electrolysis solution may disperse in mist shape at the time of opening it is desirable to open within a measuring cylinder or to cool a cell before opening and to freeze an electrolysis solution. After making ** a measuring cylinder at this time in order for a solvent to also permeate the cellular small portion which exists in the inside of a cell (in order to prevent evaporation of a solvent) and for a solvent to be able to replace a cellular portion It is desirable to give vibration with an ultrasonic cleaner etc. for 1 hour or more and for air bubbles to escape from the inside of a cell and to make

it come out.]

Let volume which subtracted the volume measured by ** from the cell total volume measured by **** be the capacity of the opening in a cell. Therefore in this invention 10% or less of cell content volume means that the capacity of an opening is 10% or less of cell content volume in the opening in a cell.

[0019] The density to be used in this invention is not less than 1.35g/cc electrolysis solution. Although a single solvent system or a mixed solvent system may be sufficient since a sacrifice fake colander is obtained and one of the characteristics is lost, it is [that it is hard to obtain the solvent which is satisfied with a single solvent of various characteristics such as a dielectric constant required for a nonaqueous electrolyte secondary battery, viscosity or the melting point and the boiling point] preferred that it is a mixed solvent system.

Therefore the easiest means that carries out density of an electrolysis solution is not less than 1.35g/cc is that density mixes not less than 1.35g/cc of not less than 1.50g/cc solvents [not less than 1.40g/cc of] more preferably. In this invention density says the density measured at 20 **.

[0020] In order that the viscosity of a solvent may affect the perviousness of an electrolysis solution it is preferred to use the solvent of 4 or less cp of viscosity as the composition solvent in preparation of the above-mentioned electrolysis solution and its solvent of 2 or less cp is more preferred. The above-mentioned viscosity says viscosity when it measures in 20 ** with an Ostwald viscometer.

[0021] As a solvent which fills above densities and viscosity For example 112-tetrafluoro ethyl-2233-tetrafluoro propyl ether (density: 1.55g [cc] /viscosity 1.27cp) 23-dihydro decafluoro pentane (density: 1.58g [cc] /viscosity: 0.67cp) etc. are mentioned.

[0022] As content in the electrolysis solution composition solvent of the above high-density solvents are based on other solvents which what is necessary is just to adjust suitably and are mixed so that the density of an electrolysis solution may be set to cc in not less than 1.35g /but. The electrolysis solution for which it has the density of a request in the composition solvent of an electrolysis solution

especially generally by making the solvent of the above-mentioned high density into not less than 35% not less than 20% by a volume ratio can be obtained.

Since when the characteristics such as a dielectric constant of a solvent itself [above-mentioned] are not the things outstanding as a composition solvent of an electrolysis solution needs to make the conventional electrolysis solution composition solvent contain to some extent 90% or less of the content is desirable at a volume ratio and is more desirable. [80% or less of]

[0023] As a conventional electrolysis solution composition solvent which can be used together with the above high-density solvents For example 12-dimethoxyethane 12-diethoxyethane propylene carbonate Although ethylene carbonate gamma-butyrolactone a tetrahydrofuran 13-dioxolane diethylene carbonate dimethyl carbonate ethyl methyl carbonate etc. are mentioned and these can also use two or more sorts simultaneously Since the density of these solvents is 1.20-1.25g/cc it is preferred to make it contain in 80% or less of range by a volume ratio in the composition solvent of an electrolysis solution.

[0024] As an electrolyte in preparation of an electrolysis solution for example LiClO_4 LiPF_6 LiBF_4 LiAsF_6 LiSbF_6 LiCF_3SO_3 $\text{LiC}_4\text{F}_9\text{SO}_3$ LiCF_3CO_2 $\text{Li}_2\text{C}_2\text{F}_4(\text{SO}_3)_2$ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ $\text{F}_{2n} \text{ of } \text{LiC}_{n+1}\text{SO}_3$ ($n \geq 2$) $\text{LiN}(\text{RfO SO}_2)_2$ [-- here -- Rf -- fluoro alkyl group] **** is independent or two or more sorts are used. LiPF_6 with a carbon numbers of two or more organic fluoride Li salt etc. are especially preferred. Although the concentration in particular of the electrolyte in an electrolysis solution is not limited Since safety will become good if concentration is made into the numerousness of 0.4 or more mol/lit is desirable 0.6 or more mol/l is more preferred and since viscosity will become low if less than 1.5 mol/lit is desirable and it is still more desirable when less than 1.0 mol/l.

[0025] Since the density of an electrolysis solution has the tendency for the injection time of an electrolysis solution to become short so that it is high it is preferred to make it high to about 1.55g/cc. Since the opening in a cell needs to increase the fill ration of a power generation element in order to attain high capacity-ization Although necessity has that it is 10% or less to cell content

volume and 5% or less of the voidage in a cell is desirable as mentioned above carrying out by about 2% is preferred on the balance of suppressing the internal pressure rise in a cell.

[0026] In this invention as positive active material for example Lithium cobalt oxide such as LiCoO_2 Although metallic sulfide such as metallic oxide such as lithium nickel oxide such as lithium manganic acid ghost such as LiMn_2O_4 and LiNiO_2 manganese dioxide vanadium pentoxide and a chromium oxidation thing or titanium disulfide and molybdenum disulfide is used What replaced these by other elements in part at the base may be used. As such an example $\text{LiNi}_{0.7}\text{Co}_{0.2}\text{Al}_{0.1}\text{O}_2$ etc. are mentioned for example. Especially when the open circuit voltage at the time of charge of LiNiO_2 , LiCoO_2 and LiMn_2O_4 etc. uses the lithium multiple oxide in which more than 4V is shown on Li standard as positive active materials since high energy density is obtained it is desirable.

[0027] An anode to the above-mentioned positive active material if needed for example For example electric conduction auxiliary agents and polyvinylidene fluoride such as scaly graphite Add binders such as polytetrafluoroethylene mix and positive electrode mixture is prepared Distribute it with a solvent make it a paste (a binder may be mixed with positive active material etc. after making it dissolve in a solvent beforehand) apply the positive electrode mixture content paste to the positive pole collector which consists of metallic foils etc. and it dries and rolls It is produced by [of a positive pole collector] forming a positive electrode mixture layer in part at least. However the manufacturing method of an anode is good by other methods without being restricted to the method of the above-mentioned illustration.

[0028] In this invention in order to attain high capacity-ization it is preferred to carry out pack density of a positive electrode mixture layer more than $2.5\text{g}/[\text{cm}]^3$ but according to this invention the infiltration speed of an electrolysis solution can be made into the case where the opening to cell content volume is bigger than 10% and an equivalent grade also in such a case. And in order to attain high

capacity-ization more the pack density of a positive electrode mixture layer. Although more than 3.0 g/cm³ is more preferred, more than 3.3 g/cm³ is still more preferred and more than 3.5 g/cm³ is the most preferred from the field of productivity. Below 4.5 g/cm³ is preferred.

[0029] Although the material used for a negative electrode is called negative electrode active material, be / what is necessary / it can be doped and / just a dope and in this invention for a lithium ion. As an example of such negative electrode active material, carbon system materials such as black lead, pyrolytic carbon, cork, glassy carbon, a baking body of an organic polymer compound, meso carbon micro beads, carbon fiber, and activated carbon are mentioned, for example. Even if the meso carbon micro beads calcinated above especially 2500 °C produce a negative electrode mixture layer with high density, its cycle characteristic is preferred from a good thing. Compounds such as an oxide which can carry out charge and discharge in the low voltage near an alloy or Li(s) such as Si, Sn, and In, etc. can be used as negative electrode active material.

[0030] When using a carbon system material as negative electrode active material, this carbon system material has a preferred thing with the following characteristic. That is, about the end-to-end dimension (d_{002}) of the (002) field, a not less than 3.5 Å thing is preferred and 3.45 Å or less is 3.4 Å or less still more preferably. As for the size (L_c) of the microcrystal of c shaft orientations, not less than 30 Å is preferred and it is not less than 250 Å still more preferably, not less than 80 Å more preferably. And as for especially the mean particle diameter of the above-mentioned carbon system material, 10-15 micrometers is preferred, 8-20 micrometers, and 99.9 % of the weight or more of purity is preferred.

[0031] A negative electrode adds the same electric conduction auxiliary agent, binder, etc. as a case of an anode to the above-mentioned negative electrode active material if needed, for example. Mix, prepare negative electrode mixture, make a solvent distribute it, and it is made a paste (since it is made to dissolve in a solvent beforehand, a binder may be mixed with negative electrode

active material etc.) The negative electrode mixture content paste is applied to the negative pole collector which consists of copper foil etc. and it dries and rolls and is produced by [of a negative pole collector] forming a negative electrode mixture layer in part at least. However the manufacturing method of a negative electrode is good by other methods without being restricted to the method of the above-mentioned illustration.

[0032] In this invention in order to attain high capacity-ization it is preferred to carry out pack density of the above-mentioned negative electrode mixture layer more than 1.0 g/cm^3 but according to this invention. Since osmosis density of the electrolysis solution to a negative electrode mixture layer can be made comparable as the former even when pack density of a negative electrode mixture layer is carried out more than 1.0 g/cm^3 this invention. If it applies when pack density of a negative electrode mixture layer is made high with more than 1.0 g/cm^3 as mentioned above especially the effect will be notably revealed. And in order to attain high capacity-ization more the pack density of a negative electrode mixture layer Although more than 1.3 g/cm^3 is more preferred more than 1.4 g/cm^3 is still more preferred and more than 1.5 g/cm^3 is the most preferred from the field of productivity below 1.65 g/cm^3 is preferred.

[0033] Although metallic foils such as aluminium foil copper foil nickel foil and stainless steel foil the thing which made those metal mesh texture etc. are used as the above-mentioned positive pole collector or a negative pole collector for example especially as a positive pole collector aluminium foil is suitable and copper foil is suitable especially as a negative pole collector.

[0034] Especially as a separator although not limited what intensity comes out enough and can moreover hold many electrolysis solutions is preferred A microporous film a nonwoven fabric etc. of the product [10-50 micrometers / hole density] made from the copolymer of 30 to 70% of product made from polyethylene the product made from polypropylene ethylene and propylene have such a viewpoint to preferred thickness.

[0035]

[Example]Belowan example is given and this invention is explained more concretely. Howeverthis invention is not limited only to those examples.

[0036]Example 11122-tetrafluoro ethyl-2233-tetrafluoro propyl ether ($\text{HCF}_2\text{CF}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{H}$)methylethyl carbonateand ethylene carbonate. The mixed solvent obtained by mixing by the volume ratio 7:2:1 was made to carry out the 1.0 mol/l dissolution of the LiPF_6 andin densityviscosity prepared the electrolysis solution of 3.6cp by cc in 1.5g /.

[0037]The mixture obtained apart from this by adding scaly graphite to LiNiO_2 as positive active material by the weight ratio 100:7 as an electric conduction auxiliary agentand mixing and the solution made to dissolve polyvinylidene fluoride in N-methyl pyrrolidone beforehand were mixedand the positive electrode mixture content paste was prepared. After passing the net of 70 meshes for this positive electrode mixture content paste and removing a big thingAfter having applied to both sides of the positive pole collector which consists of 20-micrometer-thick aluminium foil uniformlydrying to themforming a positive electrode mixture layer in them and the roller press machine cut to the prescribed dimension after compression moldingthe lead body was welded and the sheet shaped anode was produced. Thus the pack density of the positive electrode mixture layer of the produced anode was 3.3 g/cm^3 .

[0038]Nextit is a meso-carbon-micro-beads system carbon material. [(002) In 3.37 Å the end-to-end dimension (d_{002}) of a field is [the size (L_c) of the microcrystal of c shaft orientations] 950ÅThe carbon system material with the characteristic of the mean particle diameter of 15 micrometers and 99.9 % of the weight of purity] was mixed with the solution made to dissolve polyvinylidene fluoride in N-methyl pyrrolidoneand the negative electrode mixture content paste was prepared. After passing the net of 70 meshes for this negative electrode mixture content paste and removing a big thingit applies uniformlyand it dries to both sides of the negative pole collector which consists of 10-micrometer-thick band-like copper foiland a negative electrode mixture layer is formed in them. Thenafter carrying out compression molding with the roller-press machine and

cutting to a prescribed dimension the lead body was welded and the sheet shaped negative electrode was produced.

Thus the pack density of the negative electrode mixture layer of the produced negative electrode was 1.5 g/cm^3 .

[0039] After having put said sheet shaped anode on the sheet shaped above-mentioned negative electrode via the 25-micrometer-thick microporous polypropylene film winding spirally and considering it as the electrode group of spiral winding structure it inserted into the cell case with an outer diameter of 18 mm of closed-end cylindrical shape and the lead body of the anode and the negative electrode was welded.

[0040] After it poured in said electrolysis solution into a 4-ml cell case and the electrolysis solution next fully permeated the separator etc. it obturated and the nonaqueous electrolyte secondary battery of the cartridge of structure as shown in the mimetic diagram of drawing 1 was produced. The voidage in the cell of this cell was 10% to cell content volume.

[0041] When the cell shown in drawing 1 is explained 1 is the aforementioned anode and 2 is the aforementioned negative electrode. However in drawing 1 in order to avoid complicated-ization the charge collector used in production of the anode 1 or the negative electrode 2 is not illustrated. And these anodes 1 and negative electrodes 2 are spirally wound via the separator 3 are made into the electrode group of spiral winding structure and are accommodated in the cell case 5 with the above-mentioned specific electrolysis solution 4.

[0042] The cell case 5 is a product made from stainless steel as mentioned above and the insulator 6 which consists of polypropylene is arranged at the pars basilaris ossis occipitalis in advance of insertion of the electrode group of the above-mentioned spiral winding structure. The hole as the pressure inlet 7b for the obturation object 7 carrying out disc-like by the product made from aluminum and forming the thin-walled part 7a in the center section and making inter cell pressure act on the explosion proof valve 9 around the above-mentioned thin-walled part 7a is provided. And the lobe 9a of the explosion proof

valve 9 is welded to the upper surface of this thin-walled part 7a and the welded section 11 is constituted. Only the cutting plane is illustrated and as for the border line of cutting plane back the graphic display is omitted so that the thin-walled part 7a provided in the above-mentioned obturation board 7 the lobe 9a of the explosion proof valve 9 etc. may tend to carry out an understanding on a drawing. The twist is actually illustrated in the state where it is exaggerated so that an understanding on a drawing may be easy also for the welded section 11 of the thin-walled part 7a of the obturation board 7 and the lobe 9a of the explosion proof valve 9.

[0043] as for the tag block 8a nickel plate is performed to the surface by the product made from rolled steel -- an edge part -- a collar -- the shape of a hat which turned into ** is carried out.

The gas exhaust 8a is established in this tag block 8.

The explosion proof valve 9 is carrying out disc-like by the product made from aluminum.

The lobe 9a which has a tip part in the power generation element side (drawing 1 under) is formed in the center section and the thin-walled part 9b is formed and as described above the undersurface of the above-mentioned lobe 9a is welded to the upper surface of the thin-walled part 7a of the obturation board 7 and constitutes the welded section 11.

The insulating packing 10 is carrying out annular by the product made from polypropylene.

While having been arranged in the upper part of the edge part of the obturation board 7 and the explosion proof valve's 9 arranging in the upper part and insulating the obturation board 7 and the explosion proof valve 9 both gap is closed so that an electrolysis solution may not leak from between both.

The lead body 13 is a product made from aluminum said obturation board 7 and the anode 1 are connected the annular gasket 12 is a product made from polypropylene and the negative electrode 2 and the pars basilaris ossis occipitalis of the cell case 5 are connected [the insulator 14 is arranged in the upper part of

the electrode group of spiral winding structure and] by the lead body 15 made from nickel. This drawing 1 is typically illustrated in order to make structure of a cell intelligible the proportion of each members forming is not necessarily exact and the opening in a cell is not necessarily illustrated correctly either.

[0044] The nonaqueous electrolyte secondary battery of the cartridge was produced like Example 1 except having used the electrolysis solution which carried out the 1.0 mol/l dissolution and prepared LiPF_6 to the mixed solvent which mixed comparative example 1 ethylene carbonate and ethyl methyl carbonate by the volume ratio 1:2. The density of the electrolysis solution used for the cell of this comparative example 1 was 1.3g/cc and viscosity was 5.0cp.

[0045] About the above-mentioned Example 1 and the comparative example 1 an electrolysis solution pouring examination and a charge and discharge test as shown below were done.

[0046][Electrolysis solution pouring examination] The cell which is not obturated before electrolysis solution pouring with the above-mentioned composition (since the difference with Example 1 and the comparative example 1 is only an electrolysis solution before this electrolysis solution pouring.) the composition with same Example 1 and comparative example 1 -- it is -- two were prepared 3 ml of the same electrolysis solutions as what was used by Example 1 and the comparative example 1 from on the cell were poured in respectively and decompression deaeration was performed for about 10 seconds. At this time the opening in the cell after obturation is 21% of cell content volume (based on the calculation from the voidage at the time of 4-ml pouring) and since an electrolysis solution will be altogether fitted in the inside of a cell case it can be obturated as it is. If 1 ml of electrolysis solutions are further added to this and it is made for the opening in a cell to become 10% or less of cell content volume the upper part within a cell case will be covered with the electrolysis solution which cannot permeate. The time required until this electrolysis solution permeates the inside of a cell gradually and will be in the state (that is an electrolyte level below the height of the electrode group of spiral winding structure) where it can obturate

was measured. The result is shown in Table 1 as time which pouring of an electrolysis solution takes. Whether it changed into the state where it can obturate in the above-mentioned time measurement judged by viewing.

[0047]

[Table 1]

[0048] Example 1 has the substantially short time which pouring of an electrolysis solution takes compared with the comparative example 1 and according to this invention it turns out that an electrolysis solution implantation process can be shortened substantially so that clearly from the result shown in Table 1.

[0049] [Charge and discharge test] Preparing two cells of Example 1 and the comparative example 1 at a time respectively the cell which is one side respectively did the charge and discharge test in 4.1V-2.75V with the current density 1C about 1 hour after obturation measured the service capacity of the 1st charge and discharge and made it service capacity without settlement. And after settling the cell of another side for three days from obturation it measured service capacity for the charge and discharge test as ***** on the same conditions and made it service capacity with settlement respectively. The rate over service capacity with settlement of service capacity without settlement to Table 2
$$\left[\frac{\text{(service capacity without settlement)}}{\text{(service capacity with settlement)}} \times 100 \right]$$
 showed.

[0050]

[Table 2]

[0051] Since an electrolysis solution can permeate to the inside of the binder layer of an electrode in a short time even if the cell of Example 1 does not carry out prolonged settlement after obturation it will be in an usable state so that clearly from the result shown in Table 2 but. Since an electrolysis solution was not able

to permeate even the inside of the binder layer of an electrode when prolonged settlement is not carried out sufficient service capacity was not obtained but it was clear without prolonged settlement the cell's of the comparative example 1 not to become a cell which practicality has.

[0052]

[Effect of the Invention]As explained above the time which an electrolysis solution implantation process and the aging process take could be shortened and productivity was excellent in this invention and the nonaqueous electrolyte secondary battery of high capacity was able to be provided.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a sectional view showing typically an example of the nonaqueous electrolyte secondary battery concerning this invention.

[Description of Notations]

1 Anode

2 Negative electrode

3 Separator

4 Electrolysis solution

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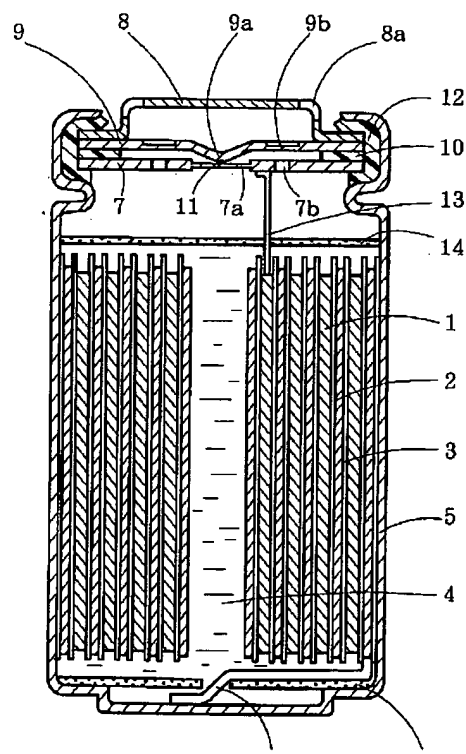
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(54)【発明の名称】 非水電解液二次電池

(57)【要約】

【課題】 電解液注入時やエージング工程に要する時間を短縮して、生産性が優れ、かつ高容量の非水電解液二次電池を提供する。

【解決手段】 シート状の正極とシート状の負極とをセパレータを介して巻回または積層した電極群を有する非水電解液二次電池において、電解液注入後の電池内の空隙を電池内容積の10%以下にし、かつ電解液の密度を1.35g/cc以上にする。



【特許請求の範囲】

【請求項1】 シート状の正極とシート状の負極とをセパレータを介して巻回または積層した電極群を有する非水電解液二次電池において、電解液注入後の電池内の空隙が電池内容積の10%以下であり、かつ電解液の密度が1.35g/cc以上であることを特徴とする非水電解液二次電池。

【請求項2】 粘度が4cp以下、密度が1.40g/cc以上の溶媒を電解液中に体積比で20%以上含有させて密度が1.35g/cc以上の電解液とした請求項1記載の非水電解液二次電池。

【請求項3】 負極の負極合剤層の充填密度が1.5g/cm³以上である請求項1または2記載の非水電解液二次電池。

【請求項4】 正極の正極合剤層の充填密度が3.3g/cm³以上である請求項1、2または3記載の非水電解液二次電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、非水電解液二次電池に関し、さらに詳しくは、生産性が優れ、かつ高容量の非水電解液二次電池に関する。

【0002】

【従来の技術】リチウム二次電池に代表される非水電解液二次電池は、高容量で、かつ高電圧、高エネルギー密度であることから、最近、急激に生産が拡大している。

【0003】従来、非水電解液二次電池の負極活物質としてはリチウムまたはリチウム合金を用いられていたが、最近、正極活物質としてLiCoO₂などのリチウム遷移金属化合物を用い、負極活物質として黒鉛、難黒鉛化炭素系材料などを用いた非水電解液二次電池が実用化されている。

【0004】この非水電解液二次電池においては、正極、負極とも、活物質を必要に応じて添加される導電助剤や結着剤などとともに有機溶媒に分散して調製した合剤含有ペーストを基材上に塗布、乾燥して合剤層を設けた後、所定厚に圧延することにより作製されている。そして、この正極と負極とをセパレータを介して巻回または積層して電極群とし、これを電池ケースに挿入した後、有機溶媒を主溶媒にした非水溶媒系の電解液を注入し、封口体により封口し、所定時間エージングすることにより、合剤層全体に電解液を浸透させ、充放電が可能なる状態にしている。

【0005】

【発明が解決しようとする課題】ところで、非水電解液二次電池の電極は、上記のように活物質などを有機溶媒でペースト状にした合剤含有ペーストを基材に塗布、乾燥して作製する塗布型電極であるため、充放電時において所望の電池容量を得るためには、合剤層中の活物質粒子間まで電解液が十分に浸透し、合剤層中の活物質のす

べてが電気化学反応に寄与する必要がある。

【0006】一方、この非水電解液二次電池を高容量化する場合、電極の体積を増大するとともに、基材上に設けられる正極および負極の合剤層の充填密度を高め、電解液の注入量も多くするなど、電池内の空隙をできる限り少なくして、電池内容積に対して発電要素の占める割合をできる限り多くする必要がある。

【0007】そして、合剤層の充填密度を高くする場合には、正極合剤層において充填密度を2.5g/cm³以上、負極合剤層において充填密度を1.0g/cm³以上にすることが提案されている（特開平4-345361号公報、特開平5-290848号公報）。

【0008】しかしながら、上記のように電極の体積を大きくし、充填密度を高くした電極群を用いた非水電解液二次電池では、電池内の空隙が少ないため、所定の電解液量を注入する際に長時間が必要になるとともに、合剤層中の空隙率も小さくなっているため、合剤層に電解液を浸透させるために行なわれる組立工程後のエージング工程にも長時間が必要になる。

【0009】特に高容量化を図るために、電解液注入後の電池内の空隙を電池内容積の20%以下と少なくした場合には、電解液注入時に所定量の電解液を一度に注入することができず、電池ケースから横溢する。そのため、電解液の注入は合剤層への電解液の浸透速度を考慮しながら、複数回に分けて注入する必要がある。しかも、非水電解液二次電池の製造工程において、律速段階となるのは電解液の注入工程とエージング工程であるため、大量生産においてはこれらの工程をできる限り短縮化することが切望されている。

【0010】従って、本発明は、上記のように高容量化を図る際の電解液注入工程やエージング工程に要する時間を短縮して、生産性が優れ、かつ高容量の非水電解液二次電池を提供することを目的とする。

【0011】

【課題を解決するための手段】本発明は、上記課題を解決すべき鋭意検討した結果なされたものであって、電解液注入後の電池内の空隙を電池内容積の10%以下にした場合でも、電解液の密度を1.35g/cc以上と高くすることにより、電解液自身の浸透性を向上させて、電解液注入工程やエージング工程に要する時間を短縮して、生産性が優れ、かつ高容量の非水電解液二次電池が得られるようにしたものである。

【0012】

【発明の実施の形態】上記密度が1.35g/cc以上の電解液を調製するにあたり、粘度が4cp以下の溶媒を含有させるときは、電解液の浸透性がより一層向上し、電解液注入工程やエージング工程に要する時間をより一層短縮することができる。

【0013】本発明を完成するに至った経過を詳しく説明すると次の通りである。